

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
20 September 2001 (20.09.2001)

PCT

(10) International Publication Number
WO 01/68572 A1

(51) International Patent Classification⁷: **C07C 11/107,**
2/32

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(21) International Application Number: PCT/EP01/02827

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(22) International Filing Date: 12 March 2001 (12.03.2001)

(25) Filing Language: English

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM,
HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK,
LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX,
MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL,
TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(26) Publication Language: English

(30) Priority Data:
MI2000A000546 17 March 2000 (17.03.2000) IT

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(84) Designated States (*regional*): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,
IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF,
CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

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Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: PROCESS FOR THE PREPARATION OF 1-HEXENE

(57) Abstract: Process for the preparation of 1-hexene consisting in effecting the oligomerization of ethylene in the presence of a catalyst comprising a vanadium complex having the formula: (arene)₂VX wherein the term arene represents benzene or mono-, di-, or tri-alkylsubstituted benzene, V is a vanadium ion with a low oxidation state, and X is an anion selected from Cl, Br and I halide ions, or from non-coordinated anions such as B(Ar)₄⁻, AlCl₄⁻, carboxylates and sulfonates.

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PROCESS FOR THE PREPARATION OF 1-HEXENE

The present invention relates to a process for the preparation of 1-hexene by the oligomerization of ethylene in the presence of vanadium complexes with a low oxidation state.

The possibility of preparing olefins with a double terminal bond by means of the oligomerization of lower olefins, for example 1-hexene by the trimerization of ethylene, is already known: for example United States patent 4,668,838 describes a process involving the use of a catalyst which comprises the reaction product between a chromium compound, a hydrocarbon derivative of partially hydrolyzed aluminum and a ligand-donor compound; European patent application 416,304 involves, in the process in question, the use of a catalytic system comprising a pyrrolidic compound of chromium and a compound of aluminum; European patent application 537,609 relates to the process

of interest which is carried out in the presence of a catalyst consisting of a complex of chromium with a polydentate ligand and an aluminoxane.

In addition to the above references, others
5 can be cited relating to the use of catalytic systems based on compounds of chromium; preparation processes of 1-hexene by the oligomerization of ethylene in the presence of these catalytic systems, however, seem to have various drawbacks
10 such as, for example, insufficient activity of the catalyst or difficulty in its preparation or the low selectivity with respect to the desired product.

The Applicant has now found that it is possible to effect the synthesis of 1-hexene by the
15 oligomerization of ethylene using a process which overcomes all the disadvantages which negatively characterize analogous processes described in the state of the art above, and which consequently
20 seem to have all the necessary industrial requisites.

The object of the invention, according to the present patent application, therefore relates to a process for the preparation of 1-hexene
25 which consists in subjecting ethylene to oli-

gomerization in the presence of a catalyst comprising a vanadium complex with a low oxidation state selected from those included in the following formula:



wherein the term arene represents benzene or mono-, di-, or tri-alkylsubstituted benzene, V is a vanadium ion with a low oxidation state, and X is an anion such as Cl, Br, I, non-coordinated
10 anions such as $\text{B}(\text{Ar})_4^-$, AlCl_4^- , carboxylates, sulfonates.

The following complexes have proved to be particularly advantageous:

bis-(mesitylene)-vanadium trifluoroacetate
15 bis-(mesitylene)-vanadium-tetraphenylborate
bis-(mesitylene)-vanadium-iodide
bis-(mesitylene)-vanadium-tetrachloroaluminate.

Vanadium arenes are already known in the art and can be prepared for example according to the
20 indications, which form an integral part of the present invention, contained in the articles of E.O. Fischer and U.S. Kogler, Chem. Ber. 90, 250 (1957), and F. Calderazzo, Inorg. Chem., 3, 810 (1964): for example according to the schemes of
25 Table 1.

In accordance with a wider aspect of the process of the present invention, these vanadium complexes can be used for the oligomerization of olefins other than ethylene, such as, for example, propylene, 1-butene, etc.: the reason the Applicant has decided to limit the description of the invention to the preparation of 1-hexene alone is simply because of the specific industrial interest in the production of this compound: any expert in the field will be able to understand from this description how to effect the oligomerization reaction starting from olefins other than ethylene, this process being included, however, in the scope of the invention according to the present patent application.

The oligomerization reaction of ethylene, according to the process of the present invention is carried out in the absence of co-catalysts, in the presence of the above vanadium compound alone or in the presence of the vanadium compound and a heterocyclic compound selected from pyrrole and derivatives.

When this heterocyclic compound is adopted, it is used in a ratio, with respect to the vanadium complex, ranging from 1 to 20: heterocyclic

compounds which can be advantageously used are pyrroles, pyrazoles, phenanthroline, pyridine and other mono and polynitrogenated derivatives.

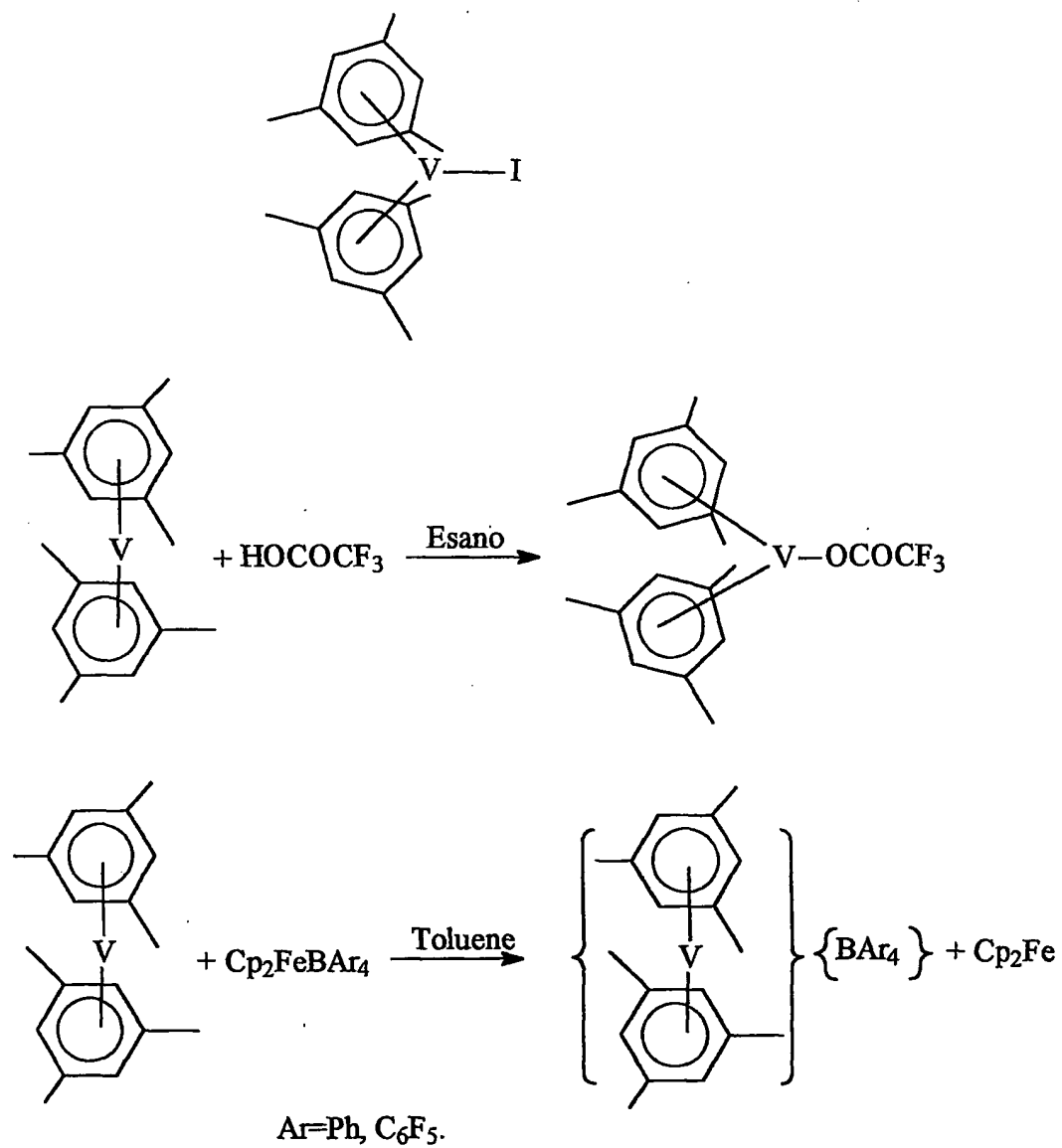
The oligomerization reaction of ethylene,
5 according to the present invention, is carried out in the presence of a solvent which is normally selected from aromatic hydrocarbons and cycloaliphatic hydrocarbons: of these, the use of toluene and cyclohexane has proved to be particularly advantageous.
10

The reaction is carried out at a temperature ranging from 0 to 150°C, preferably from 25 to 60°C, and at a pressure ranging from 1 to 100 atm., preferably from 1 to 50 atmospheres. The
15 reaction time is normally less than 36 hours, preferably from 1 to 24 hours. At the end of the reaction, 1-hexene can be separated and recovered from the reaction mixture using techniques well known to experts in the field.

20 Further details are evident from the following operative examples which are provided for a better illustration of the present invention without limiting its scope however in any way.

Table I

VANADIUM COMPLEXES



Example 1: Synthesis of $V(mes)_2(OCOCF_3)$

1.723 g of $V(mes)_2$ (5.9 mmol) and 50 ml of anhydrous and degassed n-hexane are charged under argon into a 250 ml test-tube. 0.44 ml of anhydrous trifluoroacetic acid CF_3COOH (5.9 mmol) are added to the brown solution. A brown precipitate is formed which, after 4 hours, is filtered and washed with hexane 6 times. The brown, pump-dried solid weighs 1.2 g (yield 52%).

Example 2: Synthesis of ferrocene tetraphenyl borate $Cp_2Fe(BPh_4)$

1.13 g of ferrocene Cp_2Fe (MW = 186; 6.10 mmol) are charged into a 100 ml flask and 10 ml of H_2SO_4 at 96% are slowly added dropwise. There is a substantial development of heat. 2.6 g of $Na(BPh_4)$ (MW = 342; 7.63 mmol) dissolved in 25 ml of water are slowly added dropwise to the blue solution, $Cp_2Fe(HSO_4)$. A blue precipitate is formed, which is filtered and washed with ethanol (5 x 10 ml), followed by ethyl ether (5 x 10 ml) and finally dried for a whole night with a vacuum pump and subsequently on P_2O_5 .

Example 3: Synthesis of Vanadium bis(mesitylene) tetraphenyl borate $V(mes)_2(BPh_4)$

0.350 g of $\text{Cp}_2\text{Fe}(\text{BPh}_4)$ (MW = 505; 0.7 mmoles) and 0.201 g of $\text{V}(\text{mes})_2$ (MW = 291; 0.7 mmoles) are charged under argon into a 100 ml test-tube containing 30 ml of anhydrous toluene. The mixture is left under stirring for about 4 hours; the dark solid product is filtered and dried. 0.410 g of product are obtained (yield: 96%).

Example 4

36 mg of $\text{V}(\text{mes})_2(\text{OCOCF}_3)$ (MW = 404; 0.089 mmoles) are charged under argon into a 100 ml three-necked flask. 20 ml of anhydrous and degassed toluene are added. The resulting brown solution under ethylene becomes lighter. It is left at 45°C for 24 hours. The absorption buret registers an ethylene consumption equal to 500 ml. 1 ml of the solution is removed, 1 ml of a solution of Br_2 in CCl_4 is added and GC analysis is effected.

$0.51/22.4 \text{ (l/mol)} = 0.0223 \text{ moles of ethylene used}$
up

Activity: 250.5 moles of ethylene/V moles

Selectivity: 56% to 1-hexene

Example 5

81 mg of $\text{V}(\text{mes})_2(\text{OCOCF}_3)$ (MW = 404; $2 \cdot 10^{-4}$ mmoles) are charged under argon into a 250 ml

three-necked flask. 30 ml of anhydrous and degassed toluene are added. The brown solution under ethylene becomes lighter. After 10 minutes an absorption equal to 67 ml of ethylene is obtained. After 1 hour, as there no longer seems to be any more absorption, 0.080 ml of 2,5-dimethylpyrrole (0.787 mmoles) are added, which causes a further ethylene absorption equal to 33 ml. The green solution, after a night at room temperature, becomes brown again and is analyzed via GC.

0.11/22.4 (l/mol) = 0.00446 moles of ethylene used up

Activity: 22.26 moles of ethylene/vanadium mole

Selectivity: 55% to 1-hexene

15 **Example 6**

56 mg of $V(mes)_2(OCOCF_3)$ (MW = 404; 0.138 mmoles) are charged under argon into a 100 ml three-necked flask. 0.042 ml of 2,5-dimethylpyrrole (0.408 mmoles) are added to 20 ml of distilled and degassed cyclohexane. The orange solution under ethylene darkens. It is left at 50°C for 5 hours; after 3 hours the solution is green and has absorbed 70 ml of ethylene.

GC analysis is effected.

25 0.071/22.4 (l/mol) = 0.003125 moles of ethylene

used up

Activity: 22.54 moles of ethylene/vanadium mole

Selectivity: 46% to 1-hexene

Example 7

5 64 mg of $V(mes)_2B(Ph)_4$ (MW = 610; $1.04 \cdot 10^{-4}$ moles) are charged under argon into a 100 ml three-necked flask. The mixture is dispersed in 30 ml of anhydrous toluene. The reddish-brown suspension under ethylene darkens. It is left at
10 room temperature for 20 hours. After this period of time a black suspension is formed.

In 10 minutes, 70 ml of ethylene are absorbed. It is injected into GC.

$0.071/22.4$ (l/mol) = 0.00315 moles of ethylene

15 used up

Activity: 29.8 moles of ethylene/vanadium mole

Selectivity: 66% to 1-hexene

Example 8

0.2 ml of $V(mes)_2$ at 6% in hexane (MW = 291;
20 $4.12 \cdot 10^{-5}$ moles) in 20 ml of degassed and anhydrous toluene are charged under argon into a 100 ml test-tube. 21 mg of $Cp_2Fe(BPh_4)$ (MW = 505;
 $4.12 \cdot 10^{-5}$ moles) are added to the orange solution. The orange solution is diluted up to 100 ml with
25 toluene, charged into a Buchi 300 ml glass auto-

clave and is put under 7 bars of ethylene and maintained at room temperature for 1 hour. It is observed that as ethylene is absorbed, the solution becomes turbid. The autoclave is degassed
5 and the contents discharged without diluting. 1 ml of the solution is removed, 1 ml of a solution of Br₂ in CCl₄ is added and injected into GC: only 1-hexene is present.

Activity: 605 moles of ethylene/V mole

10 Selectivity: 99% to 1-hexene

Example 9

30 mg of V(mes)₂I (MW = 418; $7.17 \cdot 10^{-5}$ moles) in 100 ml of degassed and anhydrous toluene are charged under argon into a 100 ml test-tube. The
15 orange solution is charged into a Buchi 300 ml glass autoclave, put under 7 bars of ethylene and maintained at room temperature for 1 hour. The autoclave is degassed and the contents discharged without diluting. 1 ml of the solution is re-
20 moved, 1 ml of a solution of Br₂ in CCl₄ is added and injected into GC: no olefins are present.

Activity: 0 moles of ethylene/V mole

Selectivity: 0% to 1-hexene

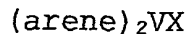
OLIGOMERIZATION TESTS OF ETHYLENE CATALYZED BY V(I)

	Catalytic precursor (mmoles)	Solvent (ml)	P (bar)	Activity (ethylene moles) / (V mole)	Selectivity (mole %)
4	V(mes) ₂ (OCOCF ₃) (0.089)	Toluene (20)	1	250.5	56
5	V(mes) ₂ (OCOCF ₃)+2,5-dimethyl pyrrole (0.2)	Toluene (30)	1	22.26	55
6	V(mes) ₂ (OCOCF ₃)+2,5-dimethyl pyrrole (0.138)	Cyclohexane (25)	1	22.54	46
7	V(mes) ₂ (BPh ₄) (0.1)	Toluene (30)	1	29.8	66
8	V(mes) ₂ 68+Cp ₂ Fe(BPh ₄) (4.12·10 ⁻⁵ moles)	Toluene (100)	7	605	99
9	V(mes) ₂ I (7.17·10 ⁻⁵ moles)	Toluene (100)	7	0	0

Tests carried out at room temperature for 1 hour.

CLAIMS

1. A process for the preparation of 1-hexene consisting in effecting the oligomerization of ethylene in the presence of a catalyst comprising a vanadium complex having
5 the formula:



wherein the term arene represents benzene or mono-, di-, or tri-alkylsubstituted benzene, V is a vanadium ion with a low oxidation state, and X is an anion selected
10 from Cl, Br and I halide ions, or from non-coordinated anions such as $\text{B}(\text{Ar})_4^-$, AlCl_4^- , carboxylates and sulfonates.

2. The process for the preparation of 1-hexene consisting in effecting the oligomerization of ethylene according
15 to the previous claim, characterized in that the reaction is carried out in the presence of a vanadium complex preferably selected from

bis-(mesitylene)-vanadium trifluoroacetate

bis-(mesitylene)-vanadium-tetraphenylborate

20 bis-(mesitylene)-vanadium-iodide

bis-(mesitylene)-vanadium-tetrachloroaluminate.

3. The process for the preparation of 1-hexene consisting in effecting the oligomerization of ethylene according to the first claim, characterized in that the reaction
25 is carried out with the additional presence of a hetero-

cyclic compound.

4. The process for the preparation of 1-hexene consisting in effecting the oligomerization of ethylene according to the previous claim, characterized in that the reaction is carried out in the presence of a heterocyclic compound preferably selected from pyrroles, substituted pyrroles, phenanthroline, pyridine.
5. The process for the preparation of 1-hexene consisting in effecting the oligomerization of ethylene according to the previous two claims, characterized in that the reaction is carried out in the presence of a heterocyclic compound in a ratio, with respect to the vanadium complex, ranging from 1 to 20.
6. The process for the preparation of 1-hexene consisting in effecting the oligomerization of ethylene according to one or more of the previous claims, characterized in that the reaction is carried out in the presence of a solvent selected from aromatic hydrocarbons and aliphatic hydrocarbons.
7. The process for the preparation of 1-hexene according to the previous claim, characterized in that the reaction is preferably carried out in the presence of a solvent selected from toluene and cyclohexene.
8. The process for the preparation of 1-hexene consisting in effecting the oligomerization of ethylene according

to one or more of the previous claims, characterized in that the reaction is carried out at a temperature less than or equal to 150°C.

9. The process for the preparation of 1-hexene according to
5 the previous claim, characterized in that the reaction is preferably carried out at a temperature ranging from 25 to 60°C.
10. The process for the preparation of 1-hexene consisting
10 in effecting the oligomerization of ethylene according to one or more of the previous claims, characterized in that the reaction is carried out at a pressure ranging from 1 to 100 atmospheres.
11. The process for the preparation of 1-hexene according
15 to the previous claim, characterized in that the reaction is preferably carried out at a pressure ranging from 1 to 50 atmospheres.
12. The process for the preparation of 1-hexene consisting
20 in effecting the oligomerization of ethylene according to one or more of the previous claims, characterized in that the reaction is carried out for times less than 36 hours.
13. The process for the preparation of 1-hexene according
25 to the previous claim, characterized in that the reaction is preferably carried out for times ranging from 1 to 24 hours.

PCT/EP 01/02827

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07C11/107 C07C2/32

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 44 36 113 A (HOECHST) 11 April 1996 (1996-04-11) claim 1 -----	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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Date of the actual completion of the international search

8 May 2001

Date of mailing of the international search report

14/05/2001

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INTERNATIONAL SEARCH REPORT

Information on patent family members

In: International Application No

Int. EP 01/02827

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 4436113 A	11-04-1996	BR 9504330 A	08-10-1996
		CA 2160101 A	11-04-1996
		CN 1129226 A	21-08-1996
		EP 0707010 A	17-04-1996
		FI 954785 A	11-04-1996
		JP 8193092 A	30-07-1996
		NO 954012 A	11-04-1996
		US 5670436 A	23-09-1997
		ZA 9508487 A	08-05-1996

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